RESEARCH OF EFFECTIVENESS OF „PLAMOSTOP“ FIRE RETARDAND AND SUITABILITY OF TESTING METHODS FOR WOOD FLAME RETARDANTS EVALUATING

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Research article

Abstract: The paper deals with testing of a water-miscible intumescent fire retardant. Experiments are conducted by thermal analysis (TG/DTG, DSC), cone calorimeter and non-standardized methods for monitoring weight loss when exposed to flame burning. Based on the experiment results and other information the most appropriate methods for testing fire retardants are reviewed. All methods by which experiments have been carried out are described. Our own method for testing fire retardants was created. It is also evaluated the effectiveness of a representative fire retardant of wood by all mentioned methods. The result of the experiment is to evaluate the suitability of each method for testing of fire retardants and evaluation fire retardant “Plamostop”.

Keywords: Testing, flame retardants, cone calorimeter, thermal analysis, burning rate.

Introduction

Flame retardants of wood are substances that impede ignition and slow the burning due to their chemical, physical or combined behaviour (Kačíková, 2011). Due to the growing of wood as a building material and as a material often used in the interior such substances have enormous use at present days. But if we want to know whether the substances have the effect of retarding agents and what it is they should be tested necessary. We can test them by different methods. All test methods should theoretically prove the effectiveness of the retarder, if it is really good one. However, not all methods provide us with the same quality of data for the evaluation of flame retardants. The question is which method would be the most appropriate for testing such substances and would allow a comparison not only within themselves but also with a clean material without flame retardants. Therefore on the basis of several experimental testing methods the aim is to determine which one is the best for comparing of the effectiveness of flame retardants. At the same time the aim is to find out what the retarding effect of the substance PLAMOSTOP Transparent is and its evaluation by all methods. PLAMOSTOP Transparent is one of the most used commercial agents with retarding effect on the combustion of wood. This flame retardant will be evaluated by thermal analysis methods, by cone calorimeter and by method formed by us.

Materials and methods

For a comprehensive evaluation of the flame retardant testing we chose four methods that will give us more detailed information about the behavior of the substance during effect of heat source. Then we can better assess the flame retardant comparing clean sample with retarded one and to determine which one of the methods gives the best information about the effectiveness of the retardant. These are the following methods:

- Thermogravimetry (TG/DTG);
- Differential scanning calorimetry (DSC);
- Cone calorimeter testing;
- Non-standardized method of continual weight loss monitoring.

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TG/DTA and DSC methods are methods of thermal analysis. Cone calorimeter is particularly used for monitoring of heat release rate on larger samples. Test procedures in these methods were performed according to appropriate standards. Last method investigating continual weight loss method is compiled by us. Terms of this method are the most similar to fire starting conditions.

Due to the evaluation of the flame retardant effect comparison between retarded and non-retarded sample we do not elaborately research in thermal analysis methods the particular actions taking place during the test. For our purposes, the evaluation will be only simple based on comparison of the measured values and curves.

Thermogravimetry

Thermogravimetry is the basic method of thermal analysis studying the weight changes taking place in the researched sample as the function of temperature. The essence of the test is heating the sample at a constant speed by a predefined temperature program while measuring the weight change as a function of temperature. The result is a thermogravimetric curve (TG curve), which graphically illustrates the dependence of the weight as a function of temperature and the derivative thermogravimetry curve (DTG curve) that shows the rate of weight loss (Brown, 1998).

Test procedure was carried out according to the standard (STN EN ISO 11358: 2000).

The samples were tested in analyzer Mettler TA 3000 processor TC 10A and thermogravimetric scales TG 50. Input parameters of the test were:

- Air flow: 200 ml/min,
- heating rate: 10 °C/min,
- temperature range (35–700) °C.

Differential Scanning Calorimetry

The principle of this method is to research the amount of energy required to maintain the same temperature of researched and reference samples which are simultaneously heated according to the set temperature program. The result of the experiment is the DSC curve that describes the ongoing endothermic and exothermic processes (Höhne et al., 2003). Test procedure was carried out according to the standard (STN ASTM E 537: 2002).

The samples were tested in thermoanalysator Mettler TA 3000 with processor TC 10A and with a measuring cell DSC 20. Input parameters of the test were:

- Air flow: 50 ml/min,
- heating rate: 10 °C/min,
- temperature range: (35–600) °C.

Cone calorimeter

Cone calorimeter is a device designed for small- sized test. It is possible to set various fire- technical characteristics by its use. The primary endpoint is the heat release rate. It is calculated on the basis of oxygen consumption measured during the test. The testing was carried out according to a standard (ISO 5660-1:2015) that describes the procedure in detail.

Testing time is reduced from the original 1800 seconds to 200 seconds since till this time most of the samples has burnt up (since the samples were thin). Therefore, for comparison of retarded and non-retarded samples for research purposes, we consider this time to be sufficient enough. Density of heat flow was 20 kW/m^2. As test material pieces were used veneers of beech wood with size of 100x100 mm and a thickness of about 1 mm. One sample was coated with fire retardants "PLAMOSTOP Transparent".

Method of continuous monitoring of weight loss

This testing method is a method designed by us for testing of flame retardants of wood and it is based on methods used in the past according to (STN 73 0862 b: 1986). When burning wood leads to the thermal degradation that is accompanied by weight loss of the testing material. At burning wood weight loss is considered as an important data. This method allows continual measurement of weight loss.

For the test there was used a simple testing device consisting of a gas bottle, torch, torch holder, the sample holder (located on the scales) and the scales. The principle of the method is an exposure of the sample to the flame at 45 ° to the horizontal surface. The flame is applied to the sample from the bottom. The flame height is 10 cm, the center of flame fall on the sample is 9 cm distant from the mouth of the burner. Testing time was 10 minutes and the actual weight was recorded every 10 s. From the results then it is possible to calculate and structure a chart of weight loss in percentage and the relative burning rate.

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Materials

At thermal analysis the samples were taken from pure beech veneer and beech veneer retarded by fire retardant. Weight of the taken samples is about 10 mg (ie. 5 mg) at the TG method (ie. DSC method).

When tested on a cone calorimeter test samples were clean beech veneer and retarded beech veneer with the size of 100x100 mm and the thickness of 1 mm.

During the method of continual monitoring of weight loss 20 samples of pure spruce wood and 10 samples of retarded spruce wood were used. Sample sizes were 200x100x10 mm. The average weight of the samples without the retardant and with the retardant is of 80 g (± 3 g).

The reason of the choice of spruce wood for testing is its frequent use in building construction. Beech veneer choice for testing on the cone calorimeter and the TG and DSC methods are experimental, because beech veneers are made from quality material and should be more homogeneous than the spruce wood itself. However, from the point of view of thermal degradation tested by thermal analysis methods, beech wood degrades comparatively as well as spruce wood (confirming by Orémusová, 2006). Such a choice of the samples should somewhat reduce of heterogeneity of wood that can affect the test results. Considering purposes of samples comparison with each other, their humidity was not measured. The samples had the same external conditions.

As a fire retardant commercial substance "PLAMOSTOP Transparent" (PST) was used for all samples. It's intumescent fire-transparent water-soluble wood coating. The chemical composition of this retarder is not public, so it is not shown here. The coating was applied to all samples in one layer (including beech veneer) on both sides.

Results

The results of all tests are presented in the form of graphs. For each test, graphs of clean samples with retarded samples are compared. As the first results are shown the results of thermal analysis methods. Fig. 1 and Fig. 2 show graphs of TG and DTG curves of pure veneers at first and then with retardant.

In the mentioned Fig. 1 and Fig. 2 we can see the TG curves that initially show similar course of weight loss. However, in the second interval we can already notice a slight decline of weight loss of retarded sample in comparison with pure one. The most significant difference is in the third interval "Step 3 analysis," where the non-retarded sample completely lost weight at 466 °C. The retarded sample withstood till up the temperatures of 674 °C.

The DTG curves initially have a similar course, too. However, the greatest rate of weight loss (in the graph they are shown as peaks) are at retarded sample smaller (it is the right axis in the graph). This can be seen particularly in the third interval "Step 3 analysis," where non-retarded sample has the highest rate of weight loss up to 0.013 mg/s which is twice in comparison with retarded sample with the highest rate of weight loss of 0.006 mg/s. The highest effect of the retarder is therefore best seen in the last phase.

In the next Fig. 3 and 4 the DSC curves are shown. These curves show us the endothermic and exothermic effects.

Furthermore, it can be observed that the resistant rest of the non-retarded sample is in the last interval negative, at the sample with the retardant the resistant rest is 1.63 %. It is assumed that, for the sample with retarder it is created mainly by residues of this retardant. However, the resistant rest is small, so the retardant does not prevent thermal degradation of the sample (due to the small thickness of the material), but it has slowed down it significantly.

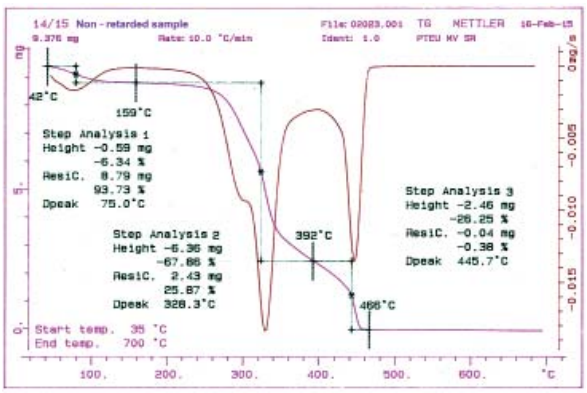

Fig. 1 The resulting TG and DTG curves of pure beech veneer samples

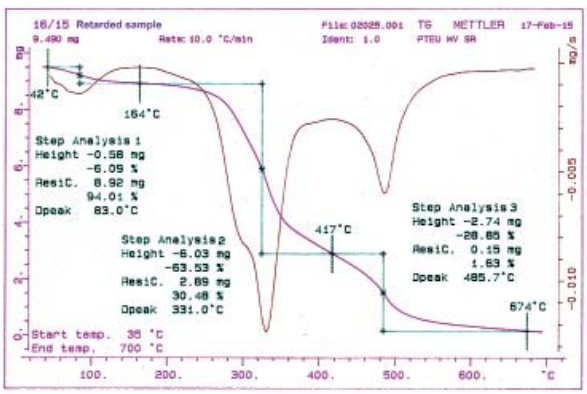

Fig. 2 The resulting TG and DTG curves of retarded beech veneer samples

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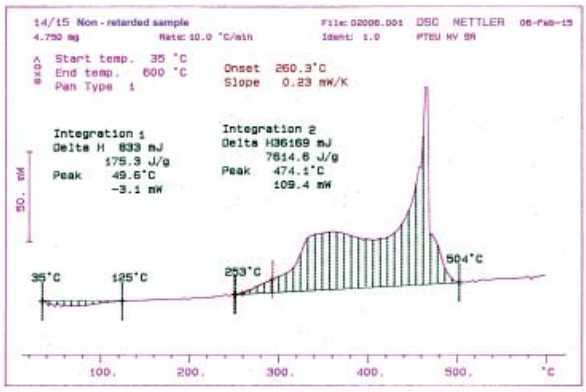

Fig. 3 DSC thermogram of non-retarded samples of beech veneer

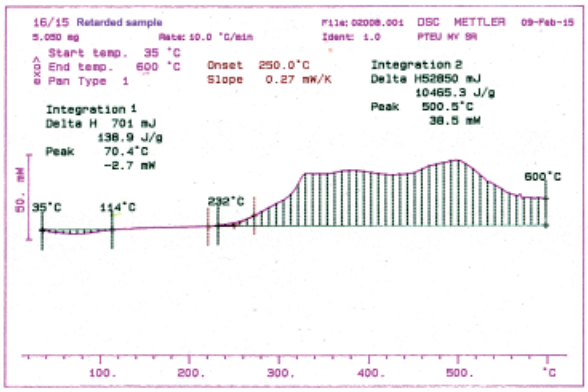

Fig. 4 DSC thermogram of retarded samples of beech veneer

The endothermic effect of retarded and non-retarded sample is quite similar in the DSC thermogram (Fig. 3 and 4). Exothermic effects, however, are quite significantly different. The effect of the retarder is particularly seen in the form of the maximum enthalpy of the reaction (peaks), which at the retarded sample reaches a maximum value of 38.5 mW at the temperature of 500.5 °C in comparison with the non-retarded sample having the maximum value of the reaction enthalpy up to 109.4 mW at 474.1 °C temperature.

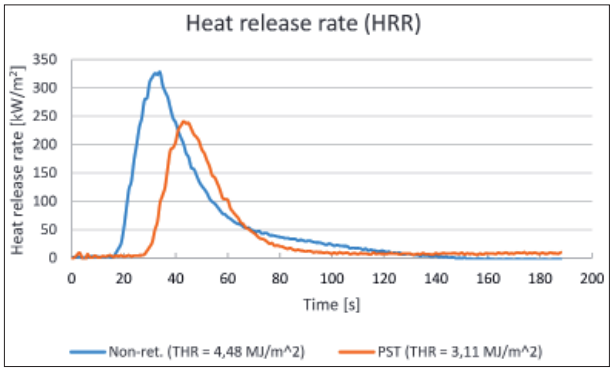

Fig. 5 Chart of heat release rate of retarded and non-retarded sample

Other very important information about the effect of the retarder are delivered to us through the results of tests on a cone calorimeter. From the measured data we have compiled a chart of heat release rate (Fig. 5).

The curves of heat release rate have from the point of view of shape similar course. The maximum heat release rate of non-retarded sample is 327 kW/m^2 in 34 s. At the retarded sample it is 237 kW/m^2 to 44 seconds. Then, in Fig. 5 we can see that the heat release rate of the retarded sample later starts and earlier ends than in the non-retarded sample. At the time of about 100 s it is approaching to zero until the end of the experiment, what means 188 s. Heat release rate of the non-retarded sample reaches zero at the time of about 150 s when the sample was completely burnt. The sight itself at the curves tell us about the lower heat release rate of the retarded samples. This means that the fire retardant has effect except of improving of fire properties also against heat release and the retarder itself does not release more heat than the sample itself. It is confirmed also by the amount of total heat release (THR – Total heat release), which is of 4.48 MJ/m^2 at the non-retarded sample, while at the sample with the retardant it is only 3.11 MJ/m^2, what is 1.37 MJ/m^2 less.

The method of weight loss provides us by the most fundamental evaluation because within all of these methods it is most approaching to the real fire conditions. In addition, it monitors the most essential parameter – weight loss. Therefore, the measurements at this method were the largest ones and more samples were used. The results are shown in the graph (Fig. 6 and 7) in the form of a curve of average percentage weight loss and average relative burning rate of non-retarded and retarded samples.

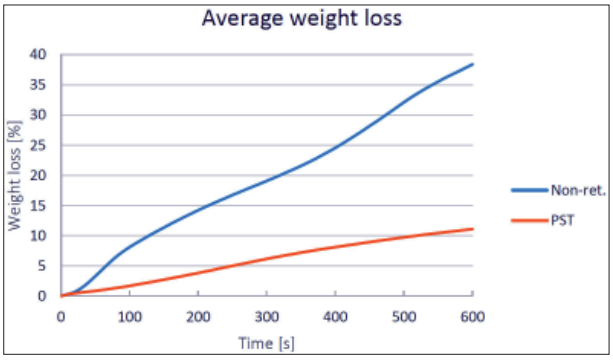

Fig. 6 Chart of average weight loss of non-retarded and retarded samples

From the outset the curve of the average weight loss of the retarded samples demonstrated a much lower weight loss than non-retarded samples. At the time of 5 minutes (half of the testing time) is the weight loss of non-retarded sample 19 %, of retarded one it is only 6 %. At the end of the experiment, so in the 10th minute the average weight loss average was 38 % for the non-retarded samples and 11 % for the retarded ones. These results demonstrate the extraordinary effectiveness of the test flame retardants.

Within the same experiment a relative burning rate, expressed in percentage, can also be observed (Fig. 7). We can observe here in which time the burning rate achieves the greatest value and thus when the greatest weight loss is set in.

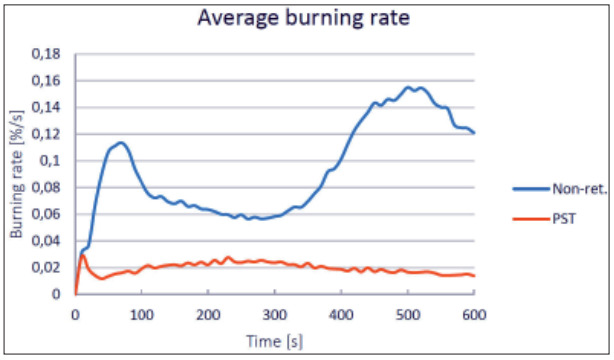

Fig. 7 Chart of average relative burning rate of non-retarded and retarded samples

In the chart we can see that the non-retarded samples had high burning rate at the beginning of the experiment, approximately up to the time of 100 s. Then the burning rate was decreasing, but after about six minutes, the burning rate was build-up almost triple. The burning rate of retarded samples was kept almost in one line for the whole period of the test, which was far lower than that of non-retarded samples, what demonstrated the efficiency of the fire retarder.

Discussion

The ability of active and high-quality flame retardants to protect against burning should be reflected in all test results. In some methods, the retarder effectiveness seems higher than in others as the results of experiments show. At the thermal analysis it is more difficult to determine the effect of the retarder, because testing occurs in only very small samples. Even at these methods, however, the effect of retarder PLAMOSTOP Transparent manifests. The tested material was beech wood. Spruce wood is more frequently used material but for thermal degradation explored by methods of thermal analysis the spruce and beech wood degrade relatively equally (as confirmed by Orémusová, 2006). TG curve shows that retarded sample completely lost their weight later as non-retarded sample. It is also related to significantly lower rate of weight loss of retarded samples in DTG curve. In the DSC method, the effect of the retarder was manifested by significantly lower value of the maximum reaction enthalpy. The effects of retarders on cellulosic materials by DSC method are dealt also by other authors (Tureková, Balog, 2003). The retarder quality was also reflected in the method of the cone calorimeter, where the maximum peak of heat release rate in retarded sample was shifted and considerably lower than for non-retarded sample. However, the biggest effect of the retarder was manifested at our method, wherein the change in weight loss of samples was examined in the time. It is particularly essential that the samples were greater than in other experiments and the conditions of this test were most resembling the real situation of a starting fire. The graph of the average weight loss showed that the studied retarder can have a huge role in the fire. This is evidenced also by the fact that the retarded samples had an average weight loss of 11 %, while non-retarded up to 38 %. It is related to the average burning rate which was significantly lower by the retarded sample all the time. The retarder effectiveness of PLAMOSTOP is also confirmed by other studies (Mitrenga Vandlíčková, Dušková, 2016).

Conclusion

The paper aimed to evaluate the retardant PLAMOSTOP Transparent using multiple testing methods, as well as to determine the most appropriate method for assessing of by retardant treated wood. From the results of all testing methods it implies that "PLAMOSTOP Transparent" has proven retarding effect and it is an appropriate means to protect wood against fire. The greatest impact of this retarder was reflected in our test method, which is similar to the method used in the past. Therefore the method of investigation of continuous weight loss at exposing to a fire retardant can be considered as the most suitable in terms of comparing the retarding effects of particular substances. In addition this method most closely mimics real fire conditions. By other methods we can find out just behaviour of the fire retardants themselves.

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